Formation of Ni-Sb Phases by Electro-Codeposition Diffusion coating

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تكوين أطوار Ni-Sb بطريقة الترسيب الكهربائي _ الانتشاري للطلاء

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الخلاصة :

تم في هذا البحث إجراء ترسيب كهربائي مزدوج لأرضية معدنية / دقائق معدنية وهذا ما يصطلح عليه (EMMC's) ثم تلى ذلك إجراء معاملة حرارية . حيث تم ترسيب أرضية نيكل / دقائق الانتيمون على سطح سبيكة الانكونيل 600 وهي احد أنواع السبائك الفائقة ذات أساس نيكل والتي تتمتع باستخدامات واسعة وقد تم تحديد التركيب المجهري لطبقة الطلاء المعالجة حرارياً باستخدام المجهر الضوئي ، حيود الأشعة السينية .

أظهرت النتائج تكون الأطوار $NiSb, Ni_3Sb, Ni_5Sb_2$ عند سطح الطلاء. كما بينت النتائج إن طور NiSb مصدر جيد لتكوين Sb_2O_4 عند تسخينه في الهواء. هذا الأوكسيد يتمتع باستقرارية جيدة عند درجات الحرارة المرتفعة.

الكلمات الرئيسية : **الطلاء المركب ، أطوار Ni-Sb ، EMMC ، سبيكة الانكونل 600 ، الطلاء الكهربائي بالنيكل - انتيمون .**

Abstract:

Electrodeposited metal matrix/metal particle composite coatings (EMMC's) were deposited, heat treated and characterized. Nickel matrix/ antimony particulate coatings deposited on Inconel 600 substrate (Ni-base superalloy) was chosen as a model system. The microstructure of the plated and heat treated coatings was characterized using light optical microscope (LOM) and X-ray diffraction analysis (XRD).

Results showed that Ni_5Sb_2, Ni_3Sb, and NiSb phases are presented in the coated layer. Further NiSb is a good source for Sb_2O_4 compound formation under open heating. This oxide has good stability at high temperatures.

Keywords: Composite Coating, Ni-Sb Phases, EMMC, Inconel 600 Alloy, Nickel Antimony Electroplating.

1. Introduction:

Coatings are often applied to enhance the surface properties of a component while maintain the mechanical properties and function of the bulk material.

Aerospace and power industries utilities rely on coatings for protection in high temperature, oxidizing environments. Currently, components such as boiler tubes and turbine blades are coated by thermal spray, weld overlay, or diffusion techniques. These coatings all have drawbacks such as oxide inclusions and porosity in thermal spray and diffusion coatings or possible high residual stress and brittle coating/ substrate interface in weld overlays that may lead to premature failure.

Thus, it is essential for industry to develop better coatings and new deposition techniques for component protection. Composite electrodeposition is an alternative method of applying an oxidation resistant surface layer. The advantages of this process include low deposition temperature, low cost, no heat affected zone, defect- free microstructure, and the ability to coat components with complex geometry (Susan et al., 2001).

Electrodeposited composite coatings maintain all the features described above, although a minimum coating thickness is required to trap the particles of the codeposited material. Successful Electro-Composite Coating System (ECCs) formed by electrolytic methods requires clean particles, typically 2 to 8 μm in size, to be dispersed uniformly throughout the electrolyte during the plating cycle. The particles must be processed so that they wet out and remain suspended in the solution, and it is important that the purity of the electrolyte is maintained (Poeton, 1988).

The technique consists in depositing the base metal on a suitable substrate from a plating bath containing the suspended solid particles. The main parameters that influence the properties of the deposits are: bath composition, pH, temperature, cathodic current density, stirring speed, and concentration of particles in the solution and size of particles (Fratari and Robi, 2003).

The objective of this work to investigate the viability to obtain Ni-Sb composite layers by electrodeposition. No work about Ni-Sb composites obtained by this route is available in literatures. Many Ni-Sb compounds were occurred depending upon the percentage of antimony as in Figure. 1 (American Society for Metals, 1979). These compounds are expected to be good source for antimony oxide Sb_2O_4 which has a polymeric structure exhibits high heat and chemical resistance, insoluble in many attacked mediums (Barnet and Wilson, 1960).

2. <u>Experimental Procedure</u>:

2.1. <u>Materials</u>:

The substrate alloy used in this study was Inconel 600 alloy (Ni- base superalloy). The nominal composition of the Inconel 600 alloy is shown in Table 1 (Spatial Metals, 1998).

The Inconel 600 alloy samples were cut into squares shape with dimensions (20 x 20 x 4 mm) and a total surface 1120 mm^2. These samples were cut from a sheet perpendicular to the rolling direction. Small whole of 2 mm diameter was drilled in each sample for holding. All surfaces, including the edges were wet ground using 120, 220, 320, 600, 800, and 1200 grit silicon carbide papers. These samples were then cleaned with distilled water, degreased with acetone and then ultrasonically cleaned for 30 minutes using ethanol as a medium. After drying, the samples were stored in polyethylene zip-lock bags.

2.2 <u>Coating Deposition</u>:

Before electrodeposition of Ni-Sb composites, Ni deposits were done according to the following steps (Graham, 1971):

1. Cold rinse.
2. Dip in 20% hydrochloric acid (1.098 sp. gr.) at 21-27 ^oC for 1 min.
3. Cold rinse.
4. Anodic etch in wood's nickel- strike bath which consisted of: 240 g/ liter $NiCl_2$ and 86 ml / liter HCl (concentration 37%) at 43 ^oC as solution temperature using deposition current density of 0.0538 amp / cm^2 for 20 sec.
5. Plate in wood's bath at 43 ^oC, using deposition current density of 0.0538 amps / cm^2 for 2 min.
6. Cold rinse.

Electrodeposition of Ni-Sb composites was performed in a typical watts bath on the Inconel 600 alloy. This work was performed in university of technology- department of production and metallurgy-corrosion lab. A nickel sulfamate electrolyte was used with the following composition: 400 g/l nickel sulfamate $Ni(NH_2SO_3)_2$, 30 g/l boric acid, 5 g/l nickel chloride ($NiCl_2$), 0.2 g/l sodium laurel sulfate (wetting agent), and 0.1 g/l coumarin (leveling agent). All of the bath compositions were mixed in 1 liter of deionized water. The bath composition is similar to that of Guglielmi (Guglielmi, 1972) and other commercial plating bath (American Society for Metals, 1979). It was found that excessive amounts of the surfactant (coumarin) can cause "foaming" of the plating bath when Sb particles are added and, therefore, minimum levels of this additive were used.

After the plating bath was prepared, the Sb powder was added. The powders are codeposited within the nickel matrix to provide for nickel antimonide formation. The antimony powder obtained from BDH Chemicals Ltd., Poole England, high purity (98.5% Sb), 8 μm max. diameter. Powder additions of 75, 150, 225, 300, 400 and 500 g/l were used in experiments.

During deposition, the Inconel 600 substrate was held vertically in the stirred stream of the electrodeposition bath. The bath was maintained at 50 ^oC and pH ≅ 4.0. It was found that deposition current density of about 4.5 amps / dm^2 produced the best results, and this current density was fixed for all coatings in the present research. Plating time of three hours was found to produce coatings of 100-125 μm thickness. To summarize Table 2 shows the major processing parameters for typical coating deposition. After deposition the samples were mounted for metallographic and / or used in heat treatment process.

2.3 Heat Treatment and X-ray Diffraction Analysis:

When as- plated Ni-Sb-EMMC coatings are exposed to high temperature, diffusion occurs between the Sb particles and the Ni matrix. The final phases present in a heat treated depend on temperature and Ni-Sb phase diagram (Fig. 1) (American Society for Metals, 1979).

To investigate nickel antimonide alloy formation, samples were heat treated in quartz tube furnace type Carbolite, manufactured by Sheffiled, England that was kept under argon atmosphere with a flow rate of 1.5 l/min. to avoid the oxidation of the underlying materials during the process. Once the inert atmosphere had been established, heating cycle is started. Typical annealing conditions were three hours at 550 ^oC follows by three hours at 800 ^oC. The argon atmosphere was maintained during all the annealing process as well as during cooling. This technique was performed in university of technology- department of production and metallurgy-heat treatment lab. Light optical microscopy observations showed that all the electrodeposits contained Sb particles dispersed in the electrodeposited nickel matrix (Fig. 2). It can be showed that the black regions observed in the nickel coating are Sb particles. The coating has constant thickness of about 125 μm, with no cracks or other defects, and good bonding with the substrate. In general, the Sb particles are approximately spherical in shape and distributed uniformly throughout the coating. The coatings are not etched to show the Sb particles distribution. The major phases on the surface are Ni_5Sb_2, Ni_3Sb, and Ni as indicated by XRD pattern (Fig. 3). On other hand the results of atomic absorption test indicated that the average antimony concentration is ≅ 29%. This test was performed in Bin Sina Company.

In order to limit the stability of nickel antimonide, coated samples were heated at 900 ^oC for more than 10 hrs in air continually. It was found that NiO was the dominate phase in addition to Ni_5Sb_2 and Ni_3Sb phases (Fig. 4). For this reason, to get NiSb phase this is more stable at higher temperatures (Fig. 1) (Barnet, 1960).It is necessary to increase the percentages of antimony at the surface by antimony electroplating. The electrolyte was used with the following composition (Graham, 1971):

Antimony trioxide Sb_2O_3	45 g/ liter
Potassium citrate	130 g/ liter
Citric acid	150 g/ liter

The bath was maintained at 55 ^{o}C and pH = 3.6. It was found practically that deposition current density of about 2.5 A/dm^2 produced the best results. Plating time of one hour was found to produce coatings of 80 μm thickness. Samples were heat treated under argon atmosphere. Typical annealing conditions were three hours at 550 ^{o}C followed by three hours at 800 ^{o}C. After annealing, the samples were argon cooled. Figure 5 showed planar view (unmounted sample). The coating layer looks homogenous with silvery appearance. XRD analyses were performed to identify the phases in the heat treated coatings. Fig. 6 shows the dominate phase was NiSb. The samples were heated in air at 900 ^{o}C for 6 hrs. The heat treated samples were surrounded with nearly white layer, this layer according to XRD analysis was Sb_2O_4 (Fig. 7).

3. <u>Results and Discussion</u>:

To determine the effect of Sb particle bath loading on the volume fraction of particles in the coatings, deposition experiments were performed with 75, 150, 225, 300, 400 and 500 g/l of powder in the bath. The relative volume of particles in the as- plated coatings determines the resultant coating composition and dictates, through the phase diagram, whether more stable antimonide formation is possible. In fact, the amount of particles in the coating increases as the bath loading increases. Therefore, the coatings deposited with 500 g/l particles bath loading were used in the heat treatment and XRD experiments presented during this research. The highest bath content of 500 g/l corresponds to only 30% by volume of particles in the bath which is equal to its percent in the deposited. For a given particle content in the bath, a higher resultant volume present is found in the coatings. When particles are dispersed into bath, they develop a positive charge due to a layer of Ni^{2+} ions on their surface. Bath stirring supplies particles at a constant rate to the substrate surface where they adhere to the relatively charged substrate (cathode).

During deposition, a steady state is thereby established in which the coating grows around the particles as new particles and fresh electrolyte are continuously supplied at the cathode surface. However, because of the electrostatic attraction, the steady state particles loading local to the surface is higher than the bulk bath loading. In summary, the results show that the composite electrodeposition techniques can be used to successfully produce Ni-Sb based composite coatings. The deposition follows the general trend of increasing coating volume percent with increased bath loading, up to approximately 500 g/l.

4. <u>Conclusions</u>:

1. The amount of particles codeposited into a nickel matrix increase as the amount of particles in the bath is increased. A maximum amount of codeposited particles is obtained at bath loading of 500 g/l. Codeposition of Sb particles into a nickel matrix produces coatings with a uniform distribution of particles and up to a bout 30% vol. particles for bath loading 500 g/l and deposition current density of 4.5 A/ dm^2.
2. Heat treatment at 800 ^{o}C for 3 hrs under argon atmosphere results in diffusion reaction between the Sb particles and nickel matrix to produce a range of Ni-Sb intermetallics compounds like Ni_5Sb_2, Ni_3Sb phases.
3. Electrodeposition of Sb followed by diffusion annealing could produce NiSb phase.
4. NiSb phase was higher heat resistance than Ni_5Sb_2 and Ni_3Sb and could be good source for Sb_2O_4 formation which has a polymeric structure exhibits high heat resistance.
5. It seems that Sb particles more easy to diffuse and reacts with Ni matrix than continuous electroplated Sb film.

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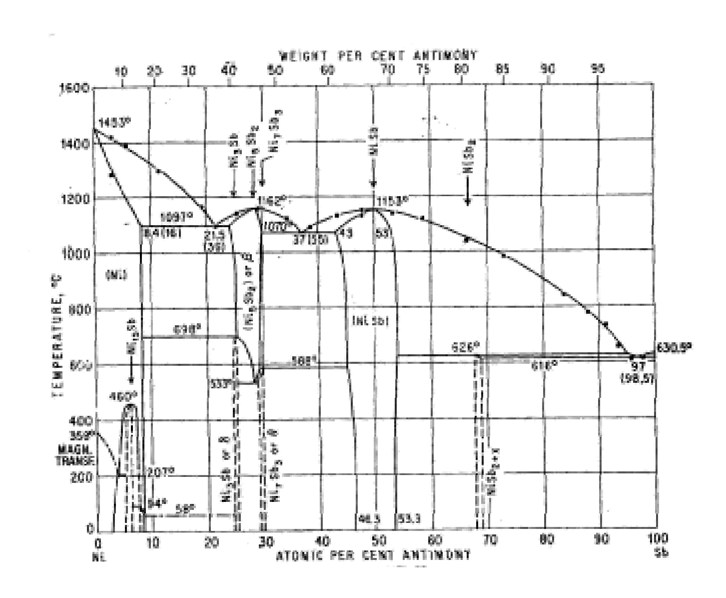


Fig. 1: Ni-Sb phase diagram (American Society for Metals, 1979)

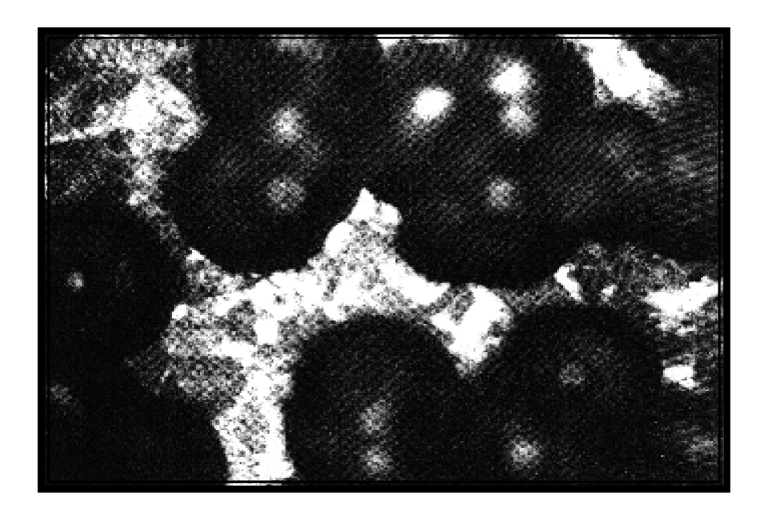


Fig. 2: LOM image of the surface of a Ni-Sb composites layer 500X.

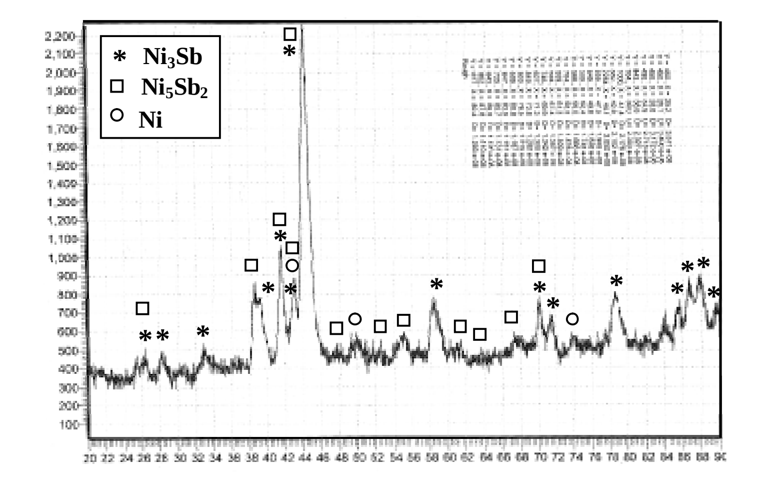


Fig. 3: Diffractograms from the surface of Inconel 600 alloy with Ni-Sb composite diffusion coated sample.

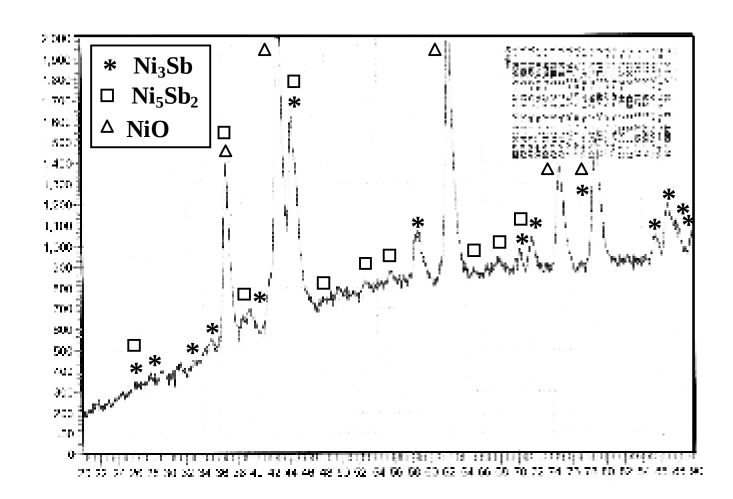


Fig. 4: Diffractograms from the surface of Inconel 600 with Ni-Sb composite diffusion coated after oxidation in air at 900 °C for 10 hrs.



Fig. 5: LOM image of Inconel 600 alloy with antimony electro-plating (Top View), 125 X.

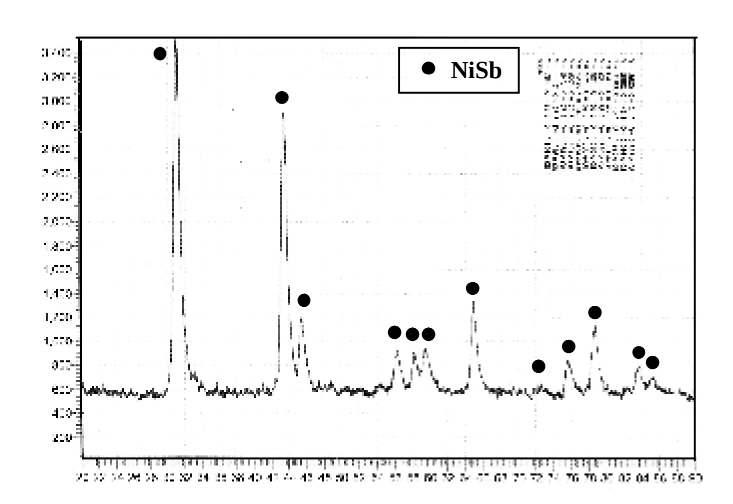


Fig. 6: Diffractograms from the surface of Inconel 600 with NiSb compound diffusion coated samples.

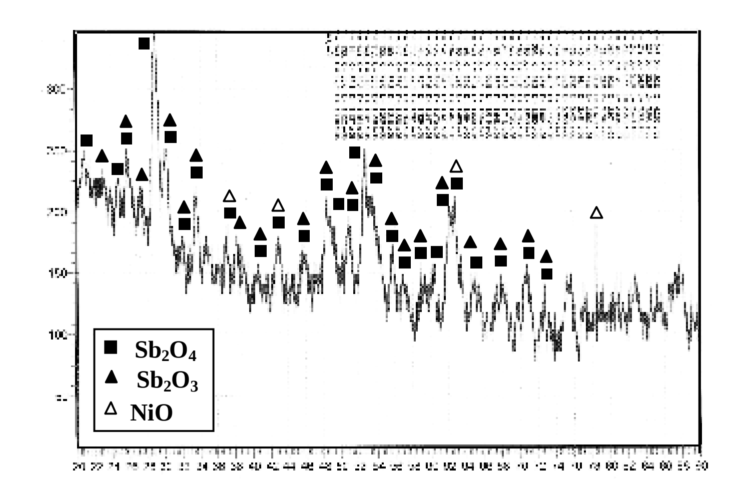


Fig. 7: Diffractograms from the surface of Inconel 600 with NiSb compound diffusion coated after oxidation in air at 900 ^{o}C for 10 hrs.

Table 1: Nominal Composition of Inconel 600 Alloy in wt. %, according to (Spatial Metals,1996)

Ni	Cr	Cu	Fe	Mn	Si	S	P	C
72.0	15.5	0.5	8.0	1.0	0.5	0.015	0.015	0.065
Min		Max		Max	Max	Max	Max	

Table 2: Major Processing Parameters for a Typical Ni-Sb EMMC Coating.

Plating Bath	**Nickel Sulfamate**
Particle loading (Sb)	500 g/l
Temp.	50 ^{o}C
pH	4.0 – 4.1
Current Density	4.5 A/dm^2
Stirring	400 RPM
Plating Time	3 hrs.